Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

THE REMOVAL OF RADIOACTIVE RADIUM (Ra^{226}) FROM PILOT-PLANT ACIDIC CHLORIDE LIQUORS, BY BATCH ADSORPTION, WITH INORGANIC AND ORGANIC ADSORBENTS - PROGRESS REPORT NO. 5

A.J. Gilmore
Extractive Metallurgy Laboratory

November 1982

Project ERP-4.4.0.2.02
Uranium Extraction - Alternative

This document is ... (CANMET)

... rapport ... (CANMET)

1 pp

ENERGY RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT ERP/MSL 82-124(TR)

INTRODUCTION

The purpose of this work was to examine Ra^{226} removal from pilot-plant chloride liquors, by batch adsorption, with organic and inorganic adsorbents. $Radium^{226}$, in solids and solution discharges from current uranium milling operations, provides a concern to the general public about the long term environmental and health effects of low-level radiation from Ra^{226}. The greater part of the Ra^{226} remains with the solid tails in the sulphate technology. With the chloride technology, the bulk of the Ra^{226} is soluble. Work projects have been underway at CANMET consequently, to evaluate the potential of chloride technology, for Ra - removal, as an alternative to the well-developed sulphate technology for the leaching of radioactive uranium ores.

Tailings pond effluents, from conventional H_2SO_4 leaching circuits, contain 600 to 1200 $pCiRa^{226}/L$. A barium chloride ($BaCl_2$) addition to effluents, performed before discharge to the water environment, precipitates a radioactive radium-barium sludge. This sludge is retained in tailings ponds or dumps within the mine property boundaries. Discharged effluents, from $BaCl_2$ precipitation, to the receiving water environment should be 10 $pCiRa^{226}/L$ or less to meet federal environmental guidelines.

$Radium^{226}$ concentrations of the order of 20,000 pCi/L, from chloride circuits, could also be removed by $BaCl_2$ precipitations, but the disposal of the wet voluminous radioactive sludge remains a problem. The isolation of Ra^{226} by adsorption on an adsorbent, then disposal of the low-level, low-volume adsorbent solids with high-level nuclear wastes would be a more manageble and responsible solution to the disposal problem. Hence, long-term monitoring of effluents for Ra^{226}, after the mine and mill operations have stopped, should not be required.

Boiler feed and drilling water, at the Denison uranium mill in the Elliot Lake area of Ontario, have been treated by cation exchange for Ra^{226} removal since February 1962[1]. Feed water, pumped from Quirke Lake to mill water softeners, has a hardness of 120 ppm at a pH of 5 to 8 including 5 to 45 $pCiRa^{226}/L$. Each drinking fountain, in the Denison mill, has attached to it a home water softener containing one cubic foot of Na-form Dowex-50 plus a brine regeneration tank. Boiler feed water, for the mill, is produced by two exchanger columns, each containing 240 cu. ft of Na-form Amberlite 1R 120.

Adsorption loadings are run to Ca-breakthrough for both boiler feed and drinking water. Effluent water quality from the exhanger columns is <1 pCiRa^{226}/L. Regeneration of all cation resin in the mill is performed with 15% brine. Desorbed Ra^{226}, in the effluent brine, is discharged to the tailings dam pond for $BaCl_2$ precipitation of the Ra^{226} as the radium-barium sulsulphate [$RaBa(SO_4)_2$] sludge.

A hydrochloric acid leach[2] or a chlorination roast-leach[3] of a radioactive uranium ore would produce chloride liquors to be treated for Ra^{226} removal. The chemical removal of Ra^{226} from chloride solutions, by cation-exchange processing, has been examined in laboratory studies. Radium^{226} removal from chloride solutions has been reported from relatively pure solutions of Ra^{226} alone, by column adsorption[4], and Ra^{226} in the presence of other cations, Ca, Mg and Fe, by batch adsorption[5] and columnar adsorption[6].

PROCEDURE

Fisher-Kendall Mixers were used in batch adsorption work to determine the removal of Ra^{226} from a pilot acidic chloride leach liquor in contact with various organic and inorganic adsorbents. Nine hundred milliliters of chloride liquor were added to 1.5 g of solid adsorbent in a 900 ml polyethylene bottle. The adsorbent and liquors were contacted on the mixer by end over end agitation overnight for 16 hours. The solids were then separated from chloride liquor by millipore filtration, using a 0.45 μm pore filter. The filtrate was dispatched to the analytical control laboratory to determine Ra^{226} concentration in solution by an alpha spectrometry method.

RESULTS

The analysis of the composite of 2nd stage HCl recycle leach liquor from a pilot-plant leach of Denison uranium ore plus washes is presented in Table 1.

Table 2 presents analytical results of filtrates produced by the batch adsorption of the various adsorbents with the HCl pilot recycle liquor containing 4820 pCiRa^{226}/L. All the adsorbents adsorbed Ra^{226} to some degree. The poorest adsorber was cassiterite (SnO_2) and the best adsorber was the Dow

Table 1 - Analysis of 2nd stage HCl recycle liquor from pilot leach of Denison Mines Ltd. ore, plus washes

Determination	Assay of HCl liquor	Determination	Assay of HCl liquor
pH	0.51	Ba	1 ppm
Ra^{226}	4820 pCi/L	K	180 ppm
U	86 ppm	Na	240 ppm
Th	35 ppm	Si	120 ppm
Fe^{total}	700 ppm	Ti	50 ppm
Fe^{3+}	210 ppm	W	<1 to < 50 ppm
Ca	52 ppm	Zr	<20 ppm
Mg	21 ppm	SO_4	960 ppm
Al	410 ppm	Free HCl	23.1 g/L (0.63N HCL)
NH_4	<10 ppm	Mn	2 ppm
PO_4	20 ppm	Sn	< 1 ppm

Adsorbent			Filtrate	Ra-removal	Solubles		Adsorbent Ld.
Name	Source	Size	$pCiRa^{226}/L$	%	Feed	Filtrate	pCiRa/g
1. Apatite	MPL*	93% - 150 m	3810	21.0	PO_4 = 20 ppm	420 ppm	606
					K = 21 ppm	22 ppm	
					Na = 240 ppm	250 ppm	
2. Bentonite	MPL* (Greece)	71% - 200 m	2610	45.9	Mg = 21 ppm	27 ppm	1350
					Na = 240 ppm	270 ppm	
					K = 180 ppm	190 ppm	
3. Bentonite	MPL* (Wyoming)	92% - 200 m	3390	29.7	Mg = 21 ppm	26 ppm	858
					Na = 24 ppm	28 ppm	
4. Biotite	MPL*	98% - 200 m	3450	28.4	Mg = 21 ppm	25 ppm	822
5. Glauconite	MPL*	99% - 100 m	4090	15.1	Fe = 210 ppm	750 ppm	438
					K = 180 ppm	200 ppm	
6. Kaolinite (Clay)	MPL*	99.9% - 100 m	4070	18.4	Al = 410 ppm	420 ppm	450
7. Ammonium Paratungstate	EML***	100% + 100 m	1250	74.1	W = <1 - <50 ppm	270-300 ppm	2142
					NH_4 = <10 ppm	22 ppm	
8. SiO_2 (Floated Powder)	Lab. Reagent	240 m	3940	18.3	Si = 120 ppm	120 ppm	528
9. Barite	Five Island N.S.**	-325 + 400 m	2870	40.5	Ba = 1 ppm	1 ppm	1170
10. Ca-Zirconia	T. Wheat, MPL*	51% - 200m	3550	26.3	Zr = < 20 ppm	< 20 ppm	762
					Ca = 52	71 ppm	
11. TiO_2	Lab. Reagent	99.6% - 150 m	4430	8.1	Ti = 50 ppm	210 ppm	234
12. Kaolin Powder	Lab. Reagent	100% + 100 m	4360	9.5	Al = 410 ppm	410 ppm	270
13. Asbestos 7R-05	Johns Mansville	As received	3680	23.7	Fe = 700 ppm	780 ppm	684
14. Fiber Flax (Glass Wool)	MPL*	As received	3400	29.5	-	-	858
15. Poplar Sawdust	Ottawa Supplier	-14 m	4030	16.4	-	-	474
16. Vermiculite	MPL*	As received	4310	10.8	Mg = 21 ppm	110 ppm	314
17. Activated Charcoal	Pittsburgh	-12 + 40 m	3740	22.4	-	-	648
18. Activated Charcoal	Norit	-8 + 20 m	4150	13.9	-	-	402
19. Adsorption Alumina (Al_2O_3)	Lab. Reagent	-80 + 200 m	3700	23.2	Al = 410 ppm	440 ppm	672
20. Meta Na-Silicate	Lab. Reagent	Crystal	3790	21.4	Si = 120 ppm	240 ppm	618
21. Amberlite IR-120	Rohm & Haas	-16 + 50 m	3520	27.0	-	-	780
22. Dowex 50W8	Dow Chemical	-20 + 50 m	3510	27.2	-	-	786
23. XF 43230 Ra-Selective Complexer	Dow Chemical	As received	790	83.6	-	-	2418
24. Pyrolucite	Tetagauché Falls. N.B. (MPL)*	63% - 400 m	3780	21.6	Mn = 2 ppm	320 ppm	624
25. Cassiterite ($Sn O_2$)	MPL*	All - 200m	4860	-0.83	Sn = < 1 ppm	4 ppm	-24

* Adsorption minerals supplied by J.A. Soles and T. Wheat of CANMET, Minerals Processing Laboratories, Ottawa.

**Supplied by Geological Surveys, Ottawa.

***A chemical compound supplied by J. Laliberté, EML. Minerals with similar composition are known.

Chemical resin exchanger XF 43230. The best compound adsorber was ammonium paratungstate, superior to barite by 1.8 times, but unfortunately, analysis indicated the compound was soluble in the 0.63 N HCl of the recycle pilot liquor. Biotite, ammonium paratungstate, bentonite, etc., adsorb Ra^{226} as good as Amberlite IR 120 and Dowex 50 exchangers. Titanium oxide was soluble in the HCl. The coarser Grecian bentonite adsorbed more Ra^{226} than the finer Wyoming bentonite. Barium in the barite mineral, and Al in kaolin powder, was stable in HCl. The calcium zirconia product was inferior to barite and bentonite as a Ra^{226}-adsorber. The glass wool adsorption indicates that glass does adsorb Ra^{226}, as reported by co-workers, as good as bentonite, but better than calcium zirconia. The Ra^{226} content of the cassiterite filtrate was slightly higher than the feed liquor. Small differences, between feed and filtrate analysis of soluble elements, are significant when the entire Table 2 is considered. About 60% of the adsorbers dissolved in the 0.63 N HCl. They are adsorption alumina, ammonium paratungstate, apatite, the 2 bentonites, biotite, asbestos cassiterite, Ca-zirconia, glauconite, kaolinite, meta Na-silicate, pyrolucite, vermiculite, and titanium oxide. Only 12% of minerals appeared to be non-soluble in the HCl liquor. The 12% included barite, kaolin powder and silicon oxide. Twenty-eight per cent of the adsorbers tested were the 3 cation exchangers, activated charcoals, fiber flax and poplar sawdust.

DISCUSSION AND CONCLUSIONS

The addition of an alkali to increase pH of recycle liquor for mineral adsorption testing would, (1) add another cation to compete with the Ra^{226} on a mineral adsorbent, (2) form precipitates and only produce another radioactive product for necessary disposal, and (3) add another reagent cost to the Ra^{226} removal program.

The 23 g free HCl/L (0.63 N HCl) dissolved most of the mineral adsorbers. The best non-soluble mineral adsorber was fine barite, but then only 40.5% of Ra^{226} was removed with a loading of 1170 $pCiRa^{226}/g$. The Dow Chemical (XF 43230) resin removed 83.6% of Ra^{226} at a loading of 2418 $pCiRa^{226}/g$. The minerals containing ions of PO_4, K, Na, Mg, Fe, Al, W, NH_4, Ca, Ti, Si, Mn and Sn were soluble in the 0.63 N HCl liquor. HCl, in addition, is a typical desorbing reagent of Ra^{226} from cation exchangers.

Barite, as one of the three insolubles, should be Ra^{226}-loaded to saturation by batch adsorption. Then attempts to desorb the Ra^{226} with pH 5.0 water should be undertaken. Possibly some freezing tests, under winter conditions, to observe any changes should be done - followed again with further desorption by a pH 5.0 aqueous mixture. These tests should indicate the stability of the Ra^{226}-barite mixture. The barite, from Five Island, N.S., should be procurable at a reasonable cost. We should be on the look-out for other available non-soluable minerals as potential adsorbents.

REFERENCES

1. E. LaRocque, Verbal communication with Chief Metallurgist, Denison Mines Ltd.; 17 May 1979.

2. K.E. Haque, B.H. Lucas and G.M. Ritcey "Hydrochloric acid leaching of an Elliot Lake uranium ore"; Division Report ERP/MSL 79-140(J), CANMET, Energy, Mines and Resources Canada; 1979.

3. J.M. Skeaff "Chlorination of uranium ore for extraction of uranium, thorium, radium and for pyrite removal"; CIM Bull 120-125; August 1979.

4. A.J. Gilmore "The removal of radioactive radium^{226} from chloride liquors by ion exchange - Progress Report"; Division Report MRP/MSL 79-154(TR); CANMET, Energy, Mines and Resources Canada; 1979.

5. A.J. Gilmore, "The removal of radioactive radium^{226} in the presence of Ca, Mg and Fe cations from chloride liquors by ion exchange - Progress Report No. 2"; Division Report ERP/MSL 81-2(TR); CANMET, Energy, Mines and Resources Canada; 1981.

6. A.J. Gilmore "The removal of radioactive radium^{226} from chloride liquors by columnar ion exchange in the presence of Ca, Mg and Fe cations - Progress Report No. 3"; Division Report ERP/MSL 81-70(TR); CANMET, Energy, Mines and Resources Canada; 1981.